Sicherite, TlAg$_2$(As,Sb)$_3$S$_6$, a new sulfosalt mineral from Lengenbach (Binntal, Switzerland): Description and structure determination

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ABSTRACT

Sicherite, TlAg$_2$(As,Sb)$_3$S$_6$, is a new mineral species from the famous sulfosalt locality at Lengenbach, Binntal, Switzerland. It occurs in small cavities in a dolomitic rock of Triassic age, associated with abundant realgar, and various other sulfosalts, mainly Tl-bearing species such as hutchinsonite, hatchite, and jentschite. Sicherite is orthorhombic, space group *Pmnb*, $Z = 4$, $a = 12.479(3)$, $b = 15.522(4)$, $c = 5.719(4)$ Å; $V = 1107.8(6)$ Å^3. The strongest powder diffraction lines [d_{obs} (Å), (*hkl*), I/I_0] are as follows: 2.822, (340, 331, 012), 100; 3.363, (301), 50; 3.118, (141), 27; 3.210 (041), 26; 3.29, (240, 311), 23; 2.540, (341), 17. Sicherite is dark metallic grey, with metallic luster, and appears completely opaque. Individual crystals reach approximately 0.4 mm, but aggregates may exceed 1–2 mm. The streak is dark brown-red, no cleavage was observed, fracture is uneven to conchoidal. Microhardness VHN$_{10}$ = 57–59 kg/mm^2, corresponding to a Mohs hardness of about 3. D_{calc} = 5.26 g/cm^3. In polished section the mineral appears pure white, with extremely weak anisotropy. Sicherite, as well as the other Tl-minerals in Lengenbach, presumably represent products of a late stage activity of Tl-As-bearing hydrothermal solutions during Alpine metamorphism. The crystal structure of sicherite was solved and refined to $R_1 = 4.62\%$. It is composed of slices of an SnS-like structure cut out parallel to (101)$_{SnS}$ and (10$\bar{1}$)$_{SnS}$ which are related by unit-cell twinning. This is similar to, but more complex than, the simpler case of emplectite. The slices are parallel to (010) of the unit cell of sicherite. They are limited by zigzag surfaces composed of short portions of ≈ (001)$_{SnS}$, and (301)$_{SnS}$ and (30$\bar{1}$)$_{SnS}$ planes, respectively. Adjacent slices are related by *n*-glide planes parallel to (010) of sicherite and interconnected via coordination polyhedra of Tl and Ag which form a very distorted PbS-like array.

INTRODUCTION

The Lengenbach quarry in Binntal (Valais Canton, Switzerland) is well known for its very uncommon sulfosalt minerals. They are mainly Pb-Cu-Ag-Tl-(As,Sb)-sulfides occurring in small cavities of white dolomitic rock of Triassic age. With the exception of some periods during the two world wars, the sulfosalt minerals have been mined almost continously for more than 150 years. It was mainly scientific interest in the sulfosalt minerals that was responsible for their exploitation. Beginning in 1833, the extraction of the minerals was conducted in the old quarry which by 1987 covered an area of approximately 30 × 20 m and reached a depth of about 20–25 m. In 1987 the old quarry was abandoned due to a lack of attractive material, and a new site was opened at a location about 20 m farther to the east, and at a higher elevation (20–25 m above the old quarry). Though the distance from the old quarry is very short, the mineralization at the new site is remarkably different. The new site is marked by much higher concentrations of Tl and As and has yielded a considerable number of rare and new mineral species. Sicherite is one of several new Tl-sulfosalts discovered

within the last decade. All the material used for this study was provided by the "Arbeitsgemeinschaft Lengenbach, AGL," a syndicate composed mainly of several Swiss museums and universities, and additionally some private individuals, who were active in Lengenbach from 1958 to 1998. Subsequently a new syndicate was founded ("Interessengemeinschaft Lengenbach, IGL") with the aim of continuing the mining of minerals at Lengenbach for research and collectors.

The mineral was named in honor of Valentin Sicher (born 1925), active member in both Lengenbach syndicates since 1963 who contributed greatly to the specimen recovery efforts.

The mineral and mineral name have been approved by the Commission on New Minerals and Mineral Names (IMA). Type material is preserved at the Department of Mineralogy, Natural History Museum, Basel, Switzerland; the samples used for X-ray, microprobe and ore microscopic studies remain at the Mineralogisch-Petrographisches Institute, University of Basel.

SAMPLE DESCRIPTION

The first sample containing the new mineral was collected in 1992 by the AGL-syndicate. It was the black metallic character that drew our attention to the small xenomorphous ore

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minerals associated with abundant realgar (most minerals from this area occurring together with realgar are Tl-sulfosalts which in general display a dark red color). A powder diffraction study of the material produced a diagram that did not match any other Lengenbach mineral. Unfortunately, the material available at that time was not suitable for a single-crystal X-ray study, and the work had to be discontinued. A second find of the same mineral (AGL number L 27′ 345) in 1996 provided appropriate crystals for a fundamental study.

Both samples containing sicherite were discovered in zones with high As contents (easily recognizable by the presence of abundant realgar). Some of the sicherite aggregates occur as inclusions in realgar. These local As enrichments also represent zones of high Tl contents. Sicherite is closely associated with Tl-minerals like hutchinsonite ($TlPbAs_5S_9$), hatchite [$TlPb(Ag,Cu)As_2S_5$], and rarely jentschite ($TlPbAs_2SbS_6$). All the Lengenbach Tl-sulfosalts are interpreted as late stage minerals formed through hydrothermal activity during Alpine metamorphism.

Sicherite samples found so far consist of aggregates up to 1 mm across. The aggregates are composed of numerous minute crystals in subparallel orientation. One nearly euhedral 0.4 mm single crystal was used for single-crystal X-ray diffraction and for the optical measurements.

PHYSICAL AND OPTICAL PROPERTIES

The physical and optical properties of sicherite are summarized in Table 1. Sicherite is elongated parallel to *a*; the morphology of the crystal is dominated by the bipyramid {141}, with the forms {001}, {010}, {031}, {301} of minor importance (Fig. 1). The axial ratio calculated from the goniometric measurement for {141} is: $a : 1 : c = 0.798 : 1 : 0.370$, in close agreement with the ratio calculated from the lattice parameters: $a : 1 : c = 0.804 : 1 : 0.368$.

The black metallic color, lack of cleavage, and uneven fracture of sicherite are very similar to the common Lengenbach minerals tennantite and seligmannite. Presumably, sicherite occurs much more frequently, but has been mistaken for other minerals.

Reflectance measurements were made from 400 to 700 nm using a Zeiss MPM800 spectrophotometer, and a SiC reflectance standard on a freshly polished grain at 23 °C (Table 2). In polished section sicherite appears pure white, with very few dark red internal reflections and extremely weak anisotropy effects. Among the Lengenbach Tl-sulfosalts, sicherite has the highest reflectivity values. Microhardness was measured on a randomly oriented surface using a Leitz Durimet microscope.

TABLE 1. Physical and optical properties of sicherite

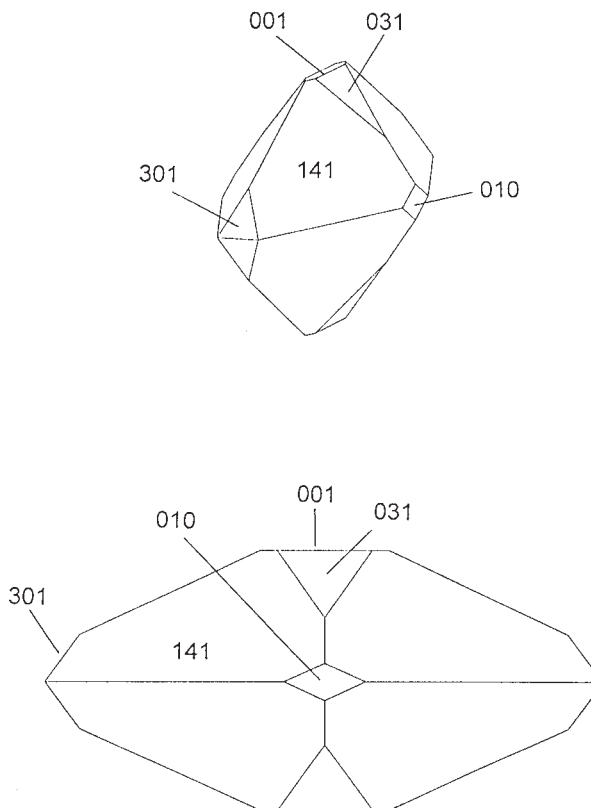|	
Morphology	bipyramidal, elongated along ***a***-axis
Forms	{141}; {031}, {001}, {010}, {301}
Color	dark grey to black, opaque
Luster	metallic
Streak	dark brown red (darker than most of the other Tl-sulfosalts)
Cleavage	not observed
Fracture	uneven to conchoidal
Twinning	not observed
Hardness	VHN_{10} = 58.3 kg/mm² (range: 57.2–59.2)
	Mohs ≤ 3 (according to VHN)
Density	5.26 g/cm³ (calculated)

FIGURE 1. Idealized drawing of a sicherite crystal based on optical goniometry.

The VHN values obtained correspond to a Mohs hardness of approximately 3 (Table 1).

CHEMICAL COMPOSITION

Preliminary semi-quantitative analyses obtained using a HITACHI SEM S-2500 scanning electron microscope showed Tl, Ag, As, Sb, S, with no additional element with atomic number ≥ 11. Quantitative analyses of the mineral were carried out using an electron microprobe (EMP). Tests for interferences yielded 2.94 wt% As on Sb metal, thus all results for As were corrected according to the equation As' [wt%] = As [wt%] − 0.0294·Sb [wt%]. Chemical data are reported in Table 3.

The analyzed sample consisted of an aggregate approximately 0.5 mm in diameter. A total of 103 analyses were obtained with a CAMECA SX-50 electron microprobe, operated at 15kV and 10 nA, with a point-focused beam. The following standards, X-ray lines, and detector crystals were used: TlSe (Tl$M\alpha$, PET), Ag metal (Ag$L\alpha$, PET), Cu metal (Cu$K\alpha$, LiF), GaAs (As$L\alpha$, TAP), Sb metal (Sb$L\alpha$, PET). Pb was sought, but was below the detection limit. The point analyses show considerable substitution of As by Sb (with negative correlation coefficient $R = -0.995$, see Fig. 2). Element distribution maps for As and Sb clearly indicate an enrichment of Sb in the apical parts of the aggregate, presumably representing a later stage of growth (Fig. 3). The As-Sb substitution extends over a wide range (from Sb/(As + Sb) = 0.14 to 0.58, with rare Sb dominant parts) suggesting the existence of an isomorphic solid

TABLE 2. Observations in reflected light

	in air	in oil
Color	pure white	pure white
Internal reflections	dark red (visible only along cracks from hardness indentations)	dark red (distinct)
Birefringence	not observed	not observed
Pleochroism	not observed	not observed
Anisotropy	extremely weak	distinct

Reflectance values

Wavelengths	R_1	R_2	imR_1	imR_2
400 nm	33.76	36.15	17.95	21.27
410	33.53	35.82	17.73	20.93
420	33.33	35.54	17.67	20.56
430	33.00	35.04	17.45	20.14
440	32.70	34.63	17.09	19.63
450	32.31	34.19	16.77	19.22
460	31.92	33.85	16.44	18.89
*470	31.43	33.43	15.98	18.41
480	30.99	33.00	15.65	18.07
490	30.54	32.62	15.22	17.64
500	30.07	32.25	14.81	17.26
510	29.59	31.80	14.49	16.95
520	29.23	31.44	14.18	16.59
530	28.88	31.08	13.89	16.29
540	28.52	30.74	13.62	15.96
*546	28.31	30.52	13.48	15.80
550	28.17	30.37	13.39	15.69
560	27.88	30.05	13.13	15.37
570	27.61	29.71	12.94	15.07
580	27.34	29.38	12.76	14.87
*589	27.10	29.11	12.54	14.56
590	27.07	29.08	12.52	14.53
600	26.79	28.75	12.30	14.34
610	26.53	28.46	12.14	14.07
620	26.24	28.15	11.90	13.84
630	26.02	27.91	11.73	13.60
640	25.76	27.68	11.54	13.43
*650	25.57	27.44	11.36	13.17
660	25.33	27.25	11.16	12.93
670	25.08	26.97	11.09	12.88
680	24.81	26.70	11.08	12.73
690	24.90	26.63	10.96	12.64
700	24.63	26.41	10.89	12.53

* = COM wavelenghts, WTiC standard.

TABLE 3. Chemical composition of sicherite

	Analyzed*	Range	Ideal†
Tl	23.63	21.63–24.77	23.36
Ag	23.98	22.60–24.76	24.66
Cu	0.22	0.08–0.43	
As	19.08	10.46–22.98	18.85
Sb	10.96	5.90–23.18	11.14
S	21.65	20.60–22.30	21.99
Total	99.53	99.00–100.65	100.00

Structural formula (normalized on 12 atoms pro formula)

Tl	1.02		1.0
Ag	1.96		2.0
Cu	0.03	$\Sigma = 1.99$	
As	2.24		2.2
Sb	0.80	$\Sigma = 3.04$	0.8
S	5.95		6.0

* Mean of 103 individual analyses (wt%).
† Theoretical composition for simplified formula (for As:Sb = 2.2/0.8).

solution series between sicherite and a hypothetical Sb end-member. However, almost all of the analyses (101 of 103) show As > Sb which justifies the attribution of sicherite to the As-rich end-member. A similar substitution, though to a much lesser degree, exists between the elements Ag and Cu. In contrast to
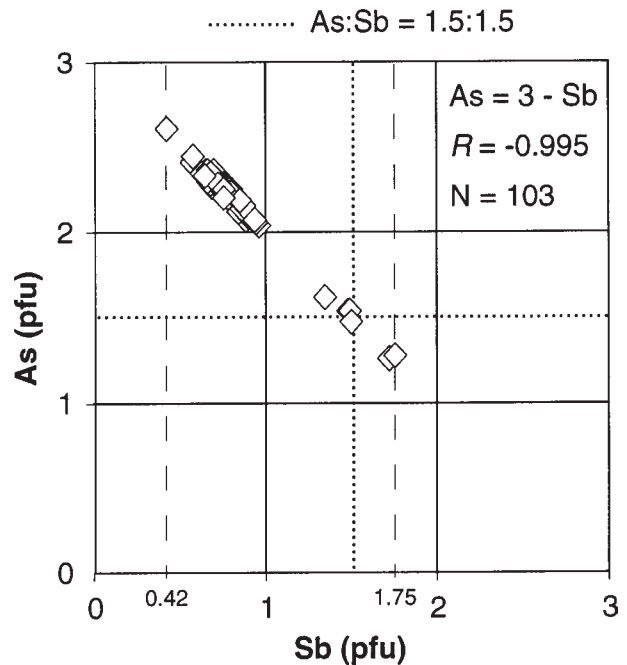
FIGURE 2. Plot of the number of As atoms per formula unit (pfu) vs. Sb atoms pfu from EMP analyses, normalized on the basis of 12 atoms.
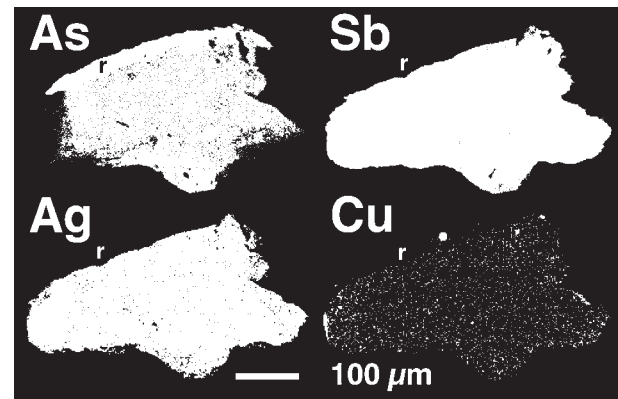
FIGURE 3. Element distribution maps for sicherite intergrown with realgar (r). The Sb-rich apical portions of the grain might represent later stages of growth. Presumably, metasomatism of the original As-rich crystal by Sb led to the observed pattern. Each map has an individual intensity scale which cannot be compared directly to the others. Analytical conditions: As$L\alpha$, Sb$L\alpha$, Ag$L\alpha$, Cu$K\alpha$, 15kV, 70nA.

the related orthorhombic Tl-mineral edenharterite, $TlPbAs_3S_6$, (Graeser and Schwander 1992), where the substitution of As by Sb leads to jentschite, $TlPbAs_2SbS_6$, (Graeser and Edenharter 1997; Berlepsch 1996), an ordered (As,Sb)-phase with a As:Sb ratio of 2:1 with lower, monoclinic symmetry, the As-Sb substitution in sicherite seems to represent a more or less complete isomorphic solid solution series. However, the observed substitutional range found in sicherite does not rule out the possibility that somewhere above Sb/(As + Sb) = 0.58 ordering may occur. The imhofite-jentschite group of Tl-minerals from Lengenbach and sicherite are closely related; this is clearly shown by mineral formulae and selected unit-cell dimensions

(Table 4), although the relations between their crystal structures are far from simple.

X-RAY ANALYSIS

Preliminary Debye-Scherrer photographs were obtained in 1993. As this material turned out to be unsuitable for single-crystal X-ray study, we decided to wait for better material. Such material was not available until 1996, when identical powder diagrams were obtained from an unknown sulfosalt phase from Lengenbach. The complete set of powder data and lattice parameters refined from d-values are reported in Table 5. Because the mineral cannot be distinguished visually from other phases, each sample used for microprobe work, structure determination, etc. was first identified by the Gandolfi method.

TABLE 4. Relationships between several Tl-sulfosalts from Lengenbach

Name	Formula	a (Å)	b (Å)	c (Å)	β (°)
Imhofite*	$(Tl,\square)_3As_8S_{13}$	8.775	24.425	11.478	108.28°
Edenharterite†	$TlPbAs_3S_6$	15.476	47.602	5.849	90
Jentschite§	$TlPbAs_2SbS_6$	8.121	23.969	5.847	107.68°
Sicherite‡	$TlAg_2As_3S_6$	15.522	12.479	5.719	90

* Burri et al. (1965).
† Graeser and Schwander (1992).
§ Graeser and Edenharter (1997).
‡ this paper (a and b parameters exchanged).

TABLE 5. Powder-diffraction data of sicherite

hkl	d_{obs}	d_{calc}*	I_{obs}†	I_{calc}§
020	7.770	7.760	9	
011	5.346	5.359	11	6
040	3.881	3.882	11	9
131	3.655	3.666	16	17
301	3.363	3.363	50	75
240		3.296		10
	3.290		23	
311		3.287		27
041	3.210	3.210	26	41
141	3.118	3.110	27	22
340		2.837		100
331	2.822	2.820	100	24
012		2.812		63
341	2.540	2.542	17	29
260		2.390		8
	2.388		8	
520		2.376		2
332	2.141	2.143	5	20
600		2.080		24
	2.070		15	
071		2.067		4
342	2.011	2.014	6	14
631		1.8285		3
181	1.8279	1.8178	<5	3
213		1.8107		2
641		1.7457		20
	1.7376		8	
471		1.7223		10
272		1.6870		15
	1.6836		<5	
602		1.6820		4
381		1.6807		6
612		1.6722		16
651	1.6536	1.6540	9	3
472		1.5278		7
	1.5239		<5	
163		1.5232		2

Note: 90 mm Debye-Scherrer camera, Fe$K\alpha$ radiation.
* d-values calculated for: a = 12.479 (3), b = 15.522 (4), c = 5.719 (4) Å (refined from powder data).
† Intensities measured by densitometer.
§ Intensities calculated from structural data (Lazy Pulverix; Yvon et al. 1977).

Given the chemical data, which show considerable substitution of As by Sb, the fact that the powder data show a very narrow variance was unexpected. This fact, too, proves that the description of the new mineral sicherite comprises the As-rich end-member exclusively.

The single-crystal study was carried out using both Weissenberg and precession techniques which indicated space groups $Pmnb$ or $P2_1nb$, of which the former was confirmed by the full structure determination. The $Pmnb$ orientation was chosen in accordance with the principle $b > a > c$ for an orthorhombic unit cell (Donnay and Ondik 1973).

X-RAY DATA COLLECTION AND STRUCTURE REFINEMENT

A small crystal fragment of sicherite was measured using a Bruker AXS four-circle diffractometer equipped with a 1000 K CCD detector and a flat graphite monochromator using Mo$K\alpha$-radiation from a fine focus sealed tube (Table 6). The SMART system of programs was used for crystal lattice determination and X-ray data collection, SAINT+ for data reduction including intensity integration, background and Lorentz polarization corrections, and SHELXTL for the structure solution and refinement (all Bruker AXS products). The program XPREP from the SHELX package was used to make an empirical absorption correction based on reflection measurements at different azimuthal angles. From the proposed space groups $Pmnb$ and $P2_1nb$ the centrosymmetric space group $Pmnb$ was chosen consistent with the orthorhombic symmetry of the lattice and intensity statistics ($|E^2–1| = 0.912$).

TABLE 6. Summarized data collection and refinement parameters for sicherite

X-ray power	40 kV, 35 mA
Temperature	293 K
Detector to sample distance	6.0 cm
Active detection area	6.25 x 6.25 cm^2
Resolution	512 x 512 pixels
Sample size	0.14 x 0.05 x 0.04 mm^3
Exposures	2880
Rotation width per frame	0.3°
Measuring time	60 s
Coverage of possible reflections	90.1%
Average redundancy	5.4
Maximum covered 2Θ	72.84° (d = 0.60 Å)
Miller index limits	h: ± 25; k: –20, +16; l: –3, +8
Measured reflections	14133
Observed reflections	13203
Unique reflections	2617
Reflections > 2 σ(I)	1599
R_{int} before absorption correction	17.64%
R_{int} after absorption correction	12.59%
Min., max. transmission factors	3.5%, 9.1%
R_σ	9.58%
Number of l.s. parameters	79
Goof	1.000
R_1 ($F_o > 4\sigma[F_o]$)	4.62%
R_1 (all data)	9.16%
wR_2 (on F_o^2)	9.65%

$R_{int} = \Sigma|F_o^2 – F_o^2(\text{mean})| / \Sigma F_o^2$
$R_\sigma = \Sigma\sigma(F_o^2) / \Sigma F_o^2$
$R_1 = \Sigma ||F_o| – |F_c|| / \Sigma|F_o|$
$wR_2 = \sqrt{(\Sigma w[F_o^2 – F_c^2]^2 / \Sigma w[F_o^2]^2)}$
Goof = $\sqrt{(\Sigma w[F_o^2 – F_c^2] / [n–p])}$
$w = 1 / (\sigma^2[F_o^2] + [0.0305 * P]^2)$
P = $(F_o^2 + 2 F_c^2) / 3$

The structure was solved by direct methods which revealed the position of the Tl atom. In subsequent refinements the positions of the Ag, As, and S atoms were deduced from difference Fourier syntheses by selecting from among the strongest maxima at appropriate distances from Tl. To account for Sb the populations on the As sites were refined allowing for As and Sb summing to full occupancy. In a later stage of the refinement the obtained site occupancies of As and Sb were fixed and their positions allowed to refine individually. The final refinement was performed with anisotropic displacement parameters for all positions and an empirical extinction coefficient. The refinement was stopped when the mean shift/esd for varied parameters dropped below 1. The highest residual peak was 3.2 e/Å^3, 1.22 Å from Tl and the deepest valley was – 5.1 e/Å^3, 0.16 Å from Tl. Fractional atomic coordinates are listed in Table 7, anisotropic displacement parameters are given in Table 8, and selected interatomic distances and angles are shown in Table 9[1].

STRUCTURE DESCRIPTION

The crystal structure of sicherite can be described as being composed of slices of SnS-like structure cut out parallel to $(101)_{SnS}$ and $(10\overline{1})_{SnS}$ which are related by unit-cell twinning. This is similar to, but more complex than, the structure of emplectite (Makovicky 1985).The slices are parallel to (010) of the unit cell of sicherite. They are limited by zigzag surfaces composed of short portions of ≈ $(001)_{SnS}$, $(301)_{SnS}$, and $(30\overline{1})_{SnS}$ planes. Adjacent slices are related by n-glide planes parallel to (010) of sicherite, and interconnected via coordination polyhedra of Tl and Ag which form a very distorted PbS-like array (Figs. 4 and 5). The slices are made up of AsS$_7$ coordination polyhedra. Layers hosting As alternate in the b direction with layers that contain Tl and Ag. The interconnection between adjacent layers with Tl and Ag is made by strong As1-S3 bonds (Fig. 5).

COORDINATION POLYHEDRA

Tl is coordinated by six S atoms in the range 3.174(2) to 3.235(2) Å that form a distorted octahedron. Considering two additional S atoms at 3.652(2) and 3.897(2) Å, the coordination polyhedron can alternatively be described as a distorted cube. The ratio V_s/V_p for coordination number (CN) 8 (where V_p is the volume of the polyhedron and V_s the volume of a sphere fit to the ligands defining the coordination polyhedron) yields a value of 2.545 which is lower than the ideal ratio of 2.7206 for a cube (Makovicky and Balić-Žunić 1998) which shows that breaking tetragonal faces into triangular significantly distorts cubic coordination.
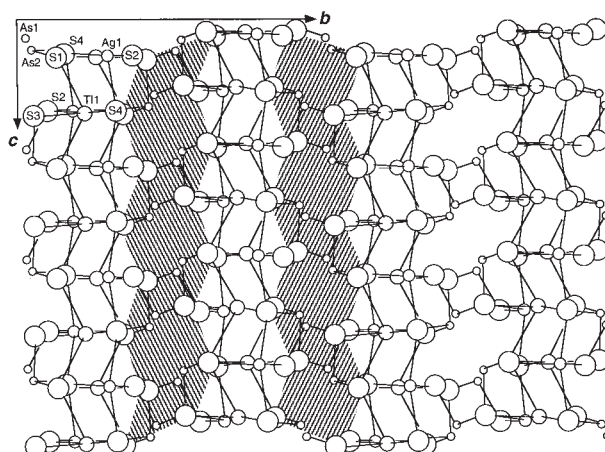

FIGURE 4. Crystal structure of sicherite projected along a. Circles in order of decreasing size represent S, Tl, Ag, and As. Shading shows two $(10\overline{1})_{SnS}$ slabs related by n-glide planes parallel to (010) and linked through coordination polyhedra of Tl and Ag that form a very distorted PbS-like array.

TABLE 7. Occupancy factors, fractional atomic coordinates, and equivalent isotropic displacement parameters for sicherite

Atom	Occ.	x/a	y/b	z/c	U_{eq}
Tl1	1	0.2500	0.23322(2)	0.87013(8)	0.03965(14)
Ag1	1	0.07814(4)	0.80769(4)	0.15465(17)	0.0586(2)
As1	0.57	0.2500	0.9641(9)	0.806(3)	0.0257(18)
Sb1	0.43	0.2500	0.9589(8)	0.796(3)	0.031(2)
As2	0.73	0.0950(2)	0.0551(4)	0.2949(10)	0.0243(10)
Sb2	0.27	0.0955(6)	0.0524(7)	0.3069(19)	0.0292(19)
S1	1	0.2500	0.14175(14)	0.3705(4)	0.0272(4)
S2	1	0.2500	0.89253(13)	0.1615(4)	0.0273(5)
S3	1	0.10710(10)	0.06197(10)	0.8866(3)	0.0273(3)
S4	1	0.97803(12)	0.16637(10)	0.3323(3)	0.0347(4)

TABLE 8. Anisotropic displacement parameters for sicherite

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tl1	0.03737(19)	0.0354(2)	0.0462(3)	0.00179(17)	0.000	0.000
Ag1	0.0418(3)	0.0397(3)	0.0944(7)	0.0171(3)	–0.0176(3)	–0.0122(2)
As1	0.019(2)	0.033(4)	0.026(3)	–0.002(2)	0.000	0.000
Sb1	0.038(3)	0.0211(17)	0.036(4)	0.003(2)	0.000	0.000
As2	0.0157(11)	0.0248(15)	0.032(2)	0.0023(12)	0.0000(9)	0.0042(9)
Sb2	0.040(3)	0.031(3)	0.017(3)	–0.0035(19)	–0.0008(18)	0.002(2)
S1	0.0218(7)	0.0299(10)	0.0299(12)	–0.0050(9)	0.000	0.000
S2	0.0239(8)	0.0258(10)	0.0322(13)	0.0023(8)	0.000	0.000
S3	0.0214(5)	0.0313(7)	0.0290(8)	0.0022(6)	–0.0013(5)	–0.0031(5)
S4	0.0265(6)	0.0294(8)	0.0484(11)	–0.0006(7)	0.0017(6)	0.0025(5)

TABLE 9. Selected interatomic distances (Å) and angles (°). In each table the distances from the central atom to the ligands are given on the diagonal, the angles between two ligands and the central atom are listed in the upper right corner, and the distances between ligands can be found in the lower left corner.

Tl1 (CN6 and *CN8*) bonded to:

	S1	S1	S3	S3	S4	S4	*S2*	*S2*
S1	3.174(2)	127.2(1)	70.0(0)	70.0(0)	98.8(0)	98.8(0)	*163.7(0)*	*65.5(0)*
S1	5.690(3)	3.177(2)	66.7(0)	66.7(0)	105.8(0)	105.8(0)	*69.1(0)*	*167.3(0)*
S3	3.645(3)	3.499(3)	3.184(2)	67.7(1)	84.9(0)	152.5(0)	*122.7(0)*	*123.1(0)*
S3	3.645(3)	3.499(3)	3.549(2)	3.184(2)	152.5(0)	84.9(0)	*122.7(0)*	*123.1(0)*
S4	4.867(2)	5.114(3)	4.333(2)	6.235(2)	3.235(2)	122.2(1)	*74.0(0)*	*69.3(0)*
S4	4.867(2)	5.114(3)	6.235(2)	4.333(2)	5.663(3)	3.235(2)	*74.0(0)*	*69.3(0)*
S2	*6.730(3)*	*3.873(3)*	*5.980(3)*	*5.980(3)*	*4.140(2)*	*4.140(2)*	*3.625(2)*	*98.2(1)*
S2	*3.873(3)*	*7.032(3)*	*6.235(3)*	*6.235(3)*	*4.091(2)*	*4.091(2)*	*5.690(3)*	*3.897(2)*

Ag1 (CN6) bonded to:

	S2	S4	S4	S4	S3	S1
S2	2.504(1)	151.1(1)	98.5(1)	96.4(1)	107.3(1)	81.8(1)
S4	4.856(2)	2.511(2)	91.7(1)	88.4(1)	101.6(1)	69.6(1)
S4	4.091(2)	3.879(2)	2.885(2)	148.4(1)	69.8(0)	102.7(1)
S4	4.140(2)	3.879(2)	5.690(3)	3.028(2)	79.3(0)	106.9(0)
S3	4.498(2)	4.333(2)	3.405(2)	3.887(2)	3.064(2)	168.7(1)
S1	3.873(3)	3.406(2)	4.867(2)	5.114(3)	6.369(2)	3.336(2)

As1 (CN7) bonded to:

	S2	S3	S3	S4	S4	S1	S2
S2	2.304(17)	97.8(5)	97.8(5)	85.6(4)	85.6(4)	160.7(5)	134.6(5)
S3	3.525(2)	2.375(10)	96.7(5)	78.9(3)	174.9(5)	70.0(3)	111.6(4)
S3	3.525(2)	3.549(2)	2.375(10)	174.9(5)	78.9(3)	70.0(3)	111.6(4)
S4	4.091(2)	3.883(2)	5.931(2)	3.562(9)	105.3(3)	105.7(3)	68.0(2)
S4	4.091(2)	5.931(2)	3.883(2)	5.663(3)	3.562(9)	105.7(3)	68.0(2)
S1	5.919(3)	3.645(3)	3.645(3)	5.786(3)	5.786(3)	3.695(16)	64.6(2)
S2	5.690(3)	5.196(3)	5.196(3)	4.140(2)	4.140(2)	4.024(3)	3.830(17)

Sb1 (CN7) bonded to:

	S2	S3	S3	S4	S4	S1	S2
S2	2.318(16)	95.6(4)	95.6(4)	86.8(4)	86.8(4)	156.9(5)	138.0(5)
S3	3.525(2)	2.438(9)	93.4(4)	79.4(3)	172.6(5)	69.1(3)	112.4(4)
S3	3.525(2)	3.549(2)	2.438(9)	172.6(5)	79.4(3)	69.1(3)	112.4(4)
S4	4.091(2)	3.883(2)	5.931(2)	3.505(8)	107.8(3)	106.4(3)	69.5(2)
S4	4.091(2)	5.931(2)	3.883(2)	5.663(3)	3.505(8)	106.4(3)	69.5(2)
S1	5.919(3)	3.645(3)	3.645(3)	5.786(3)	5.786(3)	3.717(15)	65.2(2)
S2	5.690(3)	5.196(3)	5.196(3)	4.140(2)	4.140(2)	4.024(3)	3.752(17)

As2 (CN7) bonded to:

	S4	S3	S1	S2	S3	S3	S4
S4	2.259(5)	95.8(2)	94.4(2)	171.5(2)	87.5(2)	84.9(2)	116.1(2)
S3	3.405(2)	2.330(6)	95.9(2)	76.4(1)	76.1(1)	172.3(2)	124.4(2)
S1	3.406(2)	3.499(3)	2.383(4)	89.8(2)	171.9(2)	76.5(1)	123.4(2)
S2	5.495(2)	3.525(2)	4.024(3)	3.251(5)	87.4(1)	103.4(1)	67.1(1)
S3	3.883(2)	3.521(2)	5.629(2)	4.498(2)	3.260(5)	111.6(2)	62.3(1)
S3	3.887(2)	5.690(3)	3.645(3)	5.196(2)	5.485(2)	3.372(6)	61.5(1)
S4	5.504(2)	5.769(2)	5.786(3)	4.140(2)	3.887(2)	3.883(2)	4.122(6)

Sb2 (CN7) bonded to:

	S4	S1	S3	S2	S3	S3	S4
S4	2.289(10)	93.4(4)	93.1(4)	168.7(4)	86.9(3)	86.0(3)	117.6(3)
S1	3.406(2)	2.390(9)	93.9(3)	90.1(3)	169.0(4)	77.8(3)	125.8(3)
S3	3.405(2)	3.499(3)	2.400(11)	75.9(3)	75.1(3)	171.5(4)	124.7(3)
S2	5.495(2)	4.024(3)	3.525(2)	3.232(10)	87.6(2)	105.3(3)	68.2(2)
S3	3.883(2)	5.629(2)	3.521(2)	4.498(2)	3.264(9)	113.2(3)	63.1(2)
S3	3.887(2)	3.645(3)	5.690(3)	5.196(3)	5.485(2)	3.305(11)	62.7(2)
S4	5.504(2)	5.786(3)	5.769(2)	4.140(2)	3.887(2)	3.883(2)	4.054(11)

Ag is linearly coordinated by two S atoms at 2.504(1) and 2.511(2) Å. Four additional S atoms in the range 2.885(2) to 3.336(2) Å complete a distorted octahedral coordination. Two AgS₆ polyhedra share a common S1-S2 edge and form mirror-related pairs extending along [100]. Adjacent pairs share common S4-S4 edges, are symmetry related by a screw-axis parallel to *a*, and form an openwork layer (010) which accommodates the TlS₈ polyhedra, which are isolated from one another.

Both As1 and As2 have three close S atoms (Table 9) that form a trigonal pyramid with As at the apex. Four distant S atoms complete the AsS₇ coordination polyhedra which in both cases can be described as a monocapped trigonal prism.

For Sb the same situation exists as for As. The refined Sb1 site is 0.098 Å away from As1, and the Sb2 site is 0.080 Å from As2. The short Sb-S distances are typically larger than

the corresponding As-S distances but still smaller than antici-pated for typical Sb-S short bonds. This is due to the strong overlap of the As and Sb positions and to the unresolved S positions belonging to the individual As and Sb polyhedra; these represent averaged S positions, common for As and Sb. All As positions contain significant amounts of Sb (Table 7). Consid-ering the variable amount of As and Sb in sicherite the formula $TlAg_2(As_{1.87}Sb_{1.13})_{\Sigma=3}S_6$, obtained from the structure refinement, agrees well with the previously obtained simplified formula $TlAg_2(As_{2.20}Sb_{0.84})_{\Sigma=3.04}S_6$ based on EMP data.

RELATIONSHIPS TO OTHER MINERALS

Although the chemical composition and the unit-cell pa-rameters suggest a possible relationship between sicherite and the hutchinsonite group of merotypes, no simple structural re-
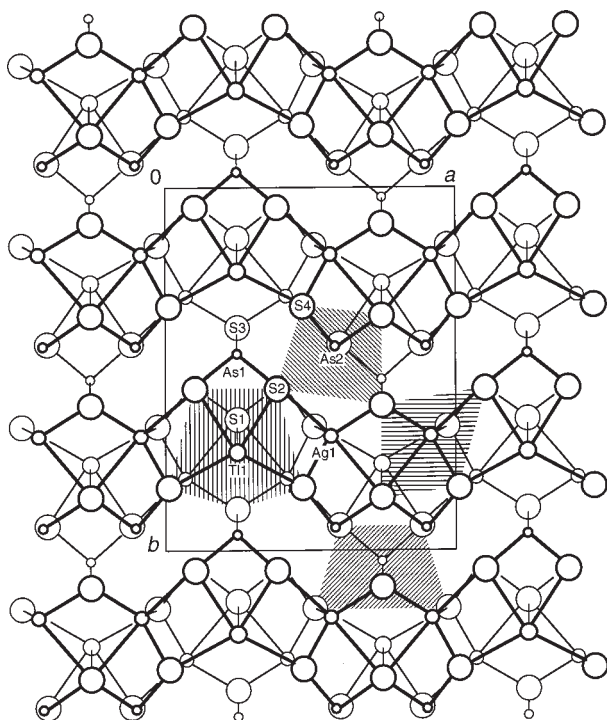
FIGURE 5. Crystal structure of sicherite projected along *c*. Circles in order of decreasing size represent S, Tl, Ag, and As. Coordination polyhedra for individual cations are shaded.

TABLE 10. Unit-cell data for sicherite, marrite, and freieslebenite

	Sicherite		Marrite	Freieslebenite
	Powder data	CCD data		
Composition	TlAg$_2$(As,Sb)$_3$S$_6$	TlAg$_2$(As,Sb)$_3$S$_6$	PbAgAsS$_3$	PbAgSbS$_3$
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pmnb*	*Pmnb*	*P2$_1$/a*	*P2$_1$/a*
a (Å)	12.479(3)	12.418(3)	7.2705(6)	7.518(1)
b (Å)	15.522(4)	15.427(3)	12.6319(4)	12.809(4)
c (Å)	5.719(4)	5.6895(13)	5.9853(3)	5.940(1)
β (°)			91.228(3)	92.25(1)
V (Å^3)	1107.8	1089.9	549.6	571.6
Z	4	4	4	4
Reference	*	*	†	‡

* This study.
† Wuensch and Nowacki (1967).
‡ Ito and Nowacki (1974).

lationship exists. In the unit-cell twinning principle, the crystal structure of sicherite shows similarities to emplectite (Portheine and Nowacki 1975). With respect to the disposition of coordination polyhedra, close relationships exist to marrite, PbAgAsS$_3$ (Wuensch and Nowacki 1967) and freieslebenite, PbAgSbS$_3$ (Ito and Nowacki 1974). These can be seen from the respective unit-cell parameters (Tab. 10), and from the projection on (001)$_\text{sicherite}$ (Fig. 5).

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